SubsurfaceTopics
INEEL Subsurface Science Initiative

Idaho National Engineering and Environmental Laboratory
June 2002 • Volume 3, Issue 2

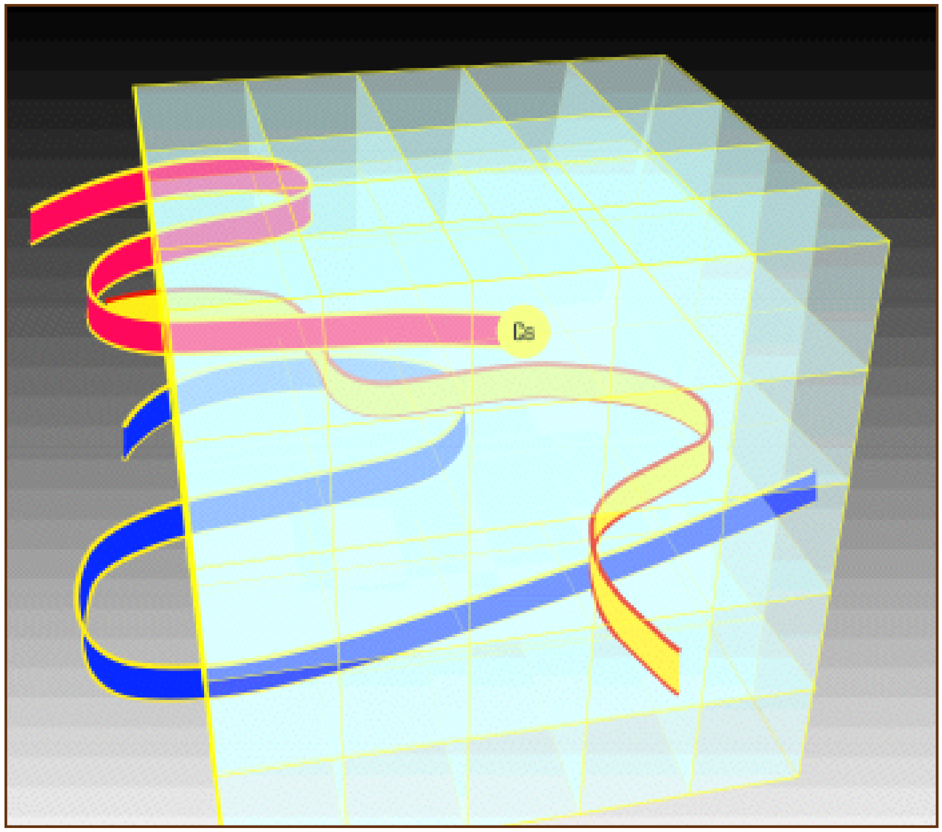
In This Issue

Initiative Director:
P. Michael Wright, Ph.D.
(208) 526-3315 or
wrigpm@inel.gov

For general information, or to be added to the mailing list, contact:
Deborah Hill
(208) 526-4723
dahill@inel.gov

SubsurfaceTopics provides technical partners and interested researchers with information and updates about the INEEL's Subsurface Science Initiative and related research. Subscribe online at http://subsurface.inel.gov/.

http://subsurface.inel.gov/



Nanocomposites
Barrier of the Future?

Is there such a thing as a "smart" barrier — one that allows water to pass through, but blocks contaminants? Two years ago, Mason Harrup, an INEEL materials scientist said,"Sure…theoretically." Finding a sturdy long-lasting material that generously passes water, sequesters contaminants, and is inexpensive to install in the subsurface is a lot to ask.

> ***"We knew we could solve the problem with expensive polymers, but... If a solution isn't economically viable, it's not really a solution."***
>
> *— M. Harrup, INEEL materials scientist and principal investigator*

But today, he and his team are on the verge of creating a permeable reactive barrier (PRB) using novel nanocomposite materials.

Harrup and his colleagues in the INEEL's separations research group are recognized as leaders in polymer chemistry, morphology, and molecular design research.He thought they had the knowledge to create a material that could meet the demanding requirements of an effective PRB (see box on next page).“The key was to find a material that could be formed in place and could pass water at a rate that

(Nanocomposites continued on page 2)

(Nanocomposites continued from page 1)

matches the hydraulic conductivity of the subsurface," said Harrup. "It would also need to maintain its mechanical strength in wet and dry conditions."

Harrup focused on nanocomposites, a combination of ceramics and polymers, which blend the strength of silicate ceramics with the formability and permeability of organic polymers. "Based on our experience, we knew they potentially had the mechanical properties needed for the job," said Harrup. One of the requirements for an effective PRB is the precursor chemicals have to be liquids that can be injected into the subsurface and catalyzed in place to form the barrier.

> ***"We needed an agent that would irreversibly bind the cesium without negatively affecting either the strength or hydraulic conductivity of the nanocomposite."***
>
> *— M. Harrup, INEEL materials scientist and principal investigator*

The team added a further condition to its solution — the materials had to be economical. "We knew we could solve the problem with expensive polymers, but we limited ourselves to water-soluble polymers that were commercially available in large quantities for under a dime per gram," said Harrup. "If a solution isn't economically viable, it's not really a solution."

The economic decision moved the team away from its initial work with an expensive polymer system, polyphosphazenes, toward a variety of inexpensive polymers, including polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc). They also targeted their research on finding a solution for one of DOE's most abundant subsurface contaminants — cesium.

Harrup's next objective was to find the best cesium-capturing agent to add to his polymer/ceramic matrix. "We needed an agent that would irreversibly bind the cesium without negatively affecting either the strength or hydraulic conductivity of the nanocomposite," said Harrup. Ammonium molybdophosphate (AMP) was chosen, though its viability for this application needed further study. Would the AMP retain its cesium-binding properties while embedded in a polymer/ceramic matrix? And how would AMP affect the nanocomposite matrix?

> ***"We knew the catalyst needed to be environmentally friendly because it would be injected. So we primarily looked at alcohol and vinegar."***
>
> *— M. Harrup, INEEL materials scientist and principal investigator*

Harrup prepared varying formulations of the AMP nanocomposite to form membrane samples that could be further tested. He and his team measured the samples' water absorption and conductivity, and cesium-capturing and leaching properties. To their surprise, they found a wide range of water-swelling

Permeable Reactive Barriers (PRB)

One approach DOE is taking to control subsurface contaminant migration is developing permanent reactive barriers (PRBs). PRBs must have the following properties:

- a tunable water passing rate to approximate the hydraulic conductivity of the subsurface environment where the PRB will be placed,
- sufficient mechanical strength (both wet and dry) to maintain barrier integrity,
- the ability to incorporate selective metal sequestration agents that remain active but do not leach from the barrier, and
- be deployable through direct injection so digging or trenching is unnecessary.

PRBs must also be reliable and have the lowest possible technology costs.

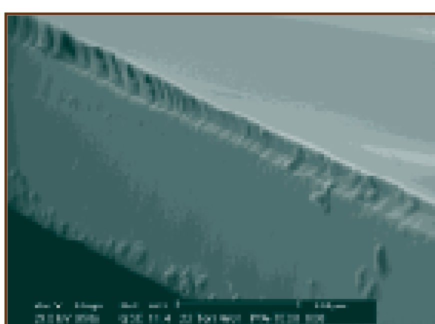


Figure 1. An SEM of a PVA nanocomposite shows the homogenous structure achieved by using acetic acid as a catalyst/solvent.

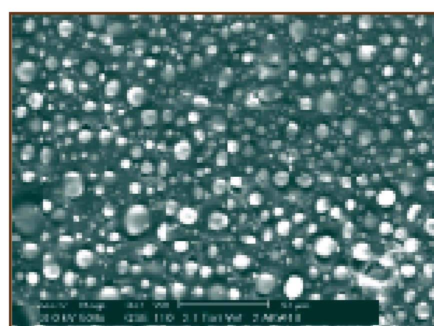


Figure 2. An SEM of a nanocomposite that phase-separated during the curing process.

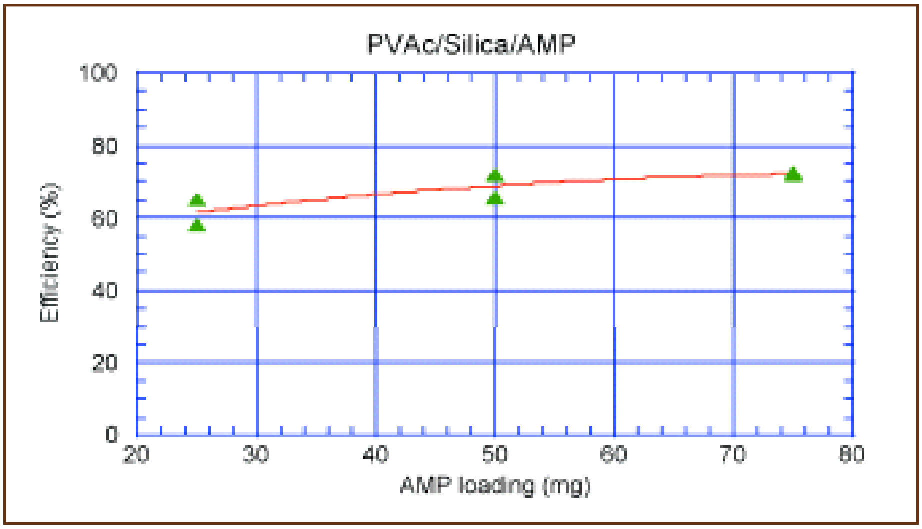


Figure 3. Cesium removal efficiency with AMP in the nanocomposite, as compared to the theoretical capacity of AMP in a solution state.

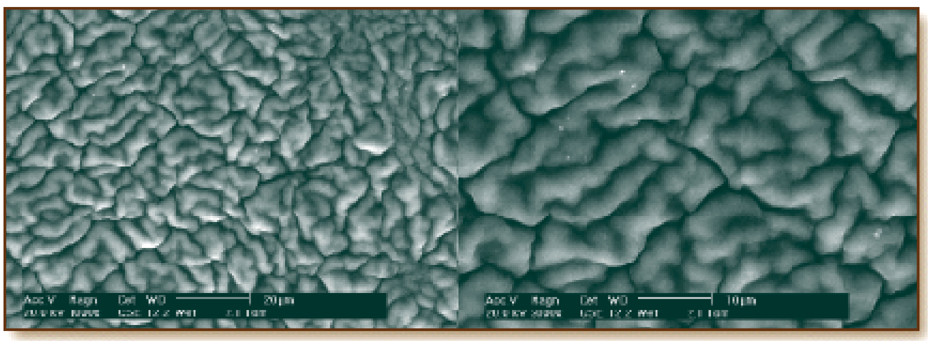


Figure 4. An ESEM of a water-swollen nanocomposite. The creases are areas with a higher ceramic density, which show less local swelling than the areas with a higher polymer component.

properties, which promised a potential match to the subsurface hydraulic conductivities at the INEEL.

Harrup had also experimented with a variety of catalysts. "We knew the catalyst needed to be environmentally friendly because it would be injected. So we primarily looked at alcohol and vinegar," said Harrup. The nanocomposites catalyzed with acetic acid had good mechanical properties. Those that used other catalysts either cracked or separated (see Figures 1 and 2).

The cesium-capturing studies conducted on the membranes had dramatic results. The cesium-capture efficiency of these membranes was about 70 percent, somewhat lower than AMP's theoretical capacity. (See Figure 3.) But some of the membranes trapped up to 97.7 percent of the removed cesium and held onto it, releasing only a few parts per billion during the leaching tests.

One concern about the membranes with good hydraulic conductivity was their mechanical toughness as they swelled so much (70 percent or more) in water (see Figure 4). So Harrup conducted another series of experiments to determine how the membranes were affected by the swelling, and by repeated wetting and drying. He also examined the possibility the material itself might be dissolving.

An examination of the nanocomposite's structure, using an environmental scanning electron microscope (ESEM), revealed no physical degradation. In addition, leaching tests indicated that less than 1 to 2 percent of the nanocomposite material was removed from the matrix after repeated wetting and drying cycles.

These test results narrowed the best candidates down to two that were particularly suitable: PVA and PVAc. The PVA nanocomposite proved to have better hydraulic conductivity; the PVAc nanocomposite had better cesium-capturing potential.

During the next phase of the project, Harrup and his team will attempt to create a blend of PVA and PVAc. "We have to find the right balance between locking cesium down and allowing water transport. By combining PVA and PVAc, we hope to create a unique offspring that has the best properties of its parents," said Harrup.

"Then we will need to examine the biotic stability of the membranes. It's hard to say whether microorganisms in the subsurface will consume the polymer component of the membrane, or if they will leave it alone. Further down the line, we might be able to integrate a biotic component where microbes and our membrane function together in some capacity."

" What amazes me is we've found a viable material with so few trials."

— M. Harrup, INEEL materials scientist and principal investigator

The team is also studying the membranes' ability to capture actinides. They have been collaborating with Robert Paine, a professor of inorganic,

(Nanocomposites continued on page 4)

(Nanocomposites continued from page 3)

organometallic and materials chemistry at the University of New Mexico, to develop innovative capturing agents specifically targeting americium and plutonium. The results of laboratory tests using these membranes are expected this summer.

So far, the INEEL team's research demonstrates that nanocomposites possess all of the required properties and attributes to be an effective PRB. What's more, though the team didn't expect to be at this stage so early in its work, the best candidates are only a few steps away from being ready for field testing.

"What amazes me is we've found a viable material with so few trials. We expected we would have to play with a lot more combinations before finding the silver bullet. Pretty soon, we'll need to pass the material to the engineers so they can make it work in the ground."

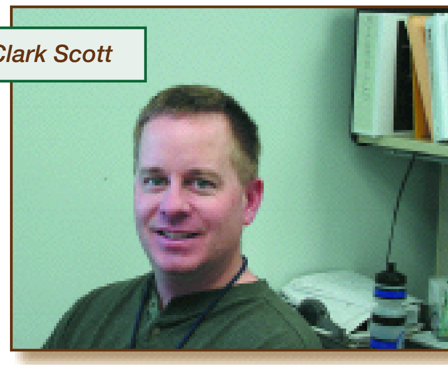
Note: This research is funded by the INEEL's Laboratory Directed Research and Development (LDRD) program. It is being conducted by: Mason K. Harrup, Ph.D.; and Michael G. Jones, Linda Polson, and Byron White (all from the INEEL). For further information, see Harrup, M.K., M. G. Jones, L. Polson, and B. White, "Synthesis, Mechanical Properties, and Cesium Sequestration Activity of Novel Polymer/Silicate Nanocomposites," Chemistry of Materials, *2002, submitted.*

Contact: Mason Harrup, Ph.D.
(208) 526-1356
harrmk@inel.gov

Fresh Ph.D.s Invigorate SSI Team

Clark Scott

Clark Scott sees himself as a generalist geophysicist with a broad range of interests and skills in earth science. "Even though I've been through a doctoral program, I still have a hard time specializing," said Scott. He has only two refereed publications left to complete his Ph.D. from the University of California at Berkeley.



Clark Scott

Nine months ago, Scott was invited to join the INEEL geophysics group to expand the Lab's geophysical capabilities. His first assignment was working in the INEEL's fossil fuels group with geophysicist Dave Weinberg, processing and interpreting data on a gas hydrate project. "I immediately found I was being tapped for my signal processing skills," said Scott.

> **"There is more work here at the INEEL than I could ever imagine. It's great."**
>
> — C. Scott, INEEL geophysicist

As a generalist geophysicist, Scott has discovered his skills are in great demand. "There is more work here at the INEEL than I could ever imagine," said Scott. "It's great." After his first assignment, he supported the development of an orbital vibrator seismic source, worked on e-tomography and consulted on several projects for the U.S. Environmental Protection Agency (EPA).

His expertise in laboratory tomography and complex resistivity monitoring will come in handy as the INEEL's Geocentrifuge Research Laboratory comes online. (See article on page 10). Developing an electronic sensor for surface or down-hole applications is one thing, but developing a sensor that can withstand 50 g's in a geocentrifuge is entirely different.

Scott's undergraduate degree is from San Diego State University. He graduated with honors and a B.S. in geology, with an emphasis in engineering and a minor in math. As an undergraduate, he helped conduct research in magneto-telluric prospecting, and wrote his thesis on micro-gravity and fault detection.

Scott also spent three summers as a teaching assistant at the Summer of Applied Geophysical Experience (SAGE), sponsored by Los Alamos National Laboratory. SAGE's emphasis on a combined methods approach was a good forum for Scott's skills. He helped instruct students in a variety of geophysical methods, including seismic reflection and refraction, gravity and magnetic surveying, resistivity, time domain electromagnetic (TDEM), very low frequency (VLF), ground penetrating radar (GPR) and the magneto-telluric method.

Scott continued pursuing his various interests while in graduate school at the University of California at Berkeley. He completed a master's thesis on the application of multivariate statistical analysis and processing of experimental seafloor magnetotelluric data, and participated in research projects studying earthquake prediction, shallow marine seismic surveying and hydro-fracture monitoring. Scott is currently completing a Ph.D. on the ultrasonic imaging of hydrate phase transition in sediments.

Contact: Clark Scott
(208) 526-2919
scotcl@inel.gov

D. Craig Cooper

Whether you call Craig Cooper a biogeochemist, geomicrobiologist or microbial geochemist, he has found his niche at the INEEL, balanced somewhere between the world of geologists, chemists and microbiologists. "I see my role as linking the fields of geology, chemistry and microbiology into a more cohesive understanding that helps DOE solve its problems and, simultaneously, advances fundamental knowledge. It really is just too cool for words."

> **" The things I've enjoyed the most about the INEEL are the dynamism of the people, and the coupling of geochemistry and microbiology."**
>
> *— C. Cooper, INEEL microbial geochemist*

After completing his Ph.D., Cooper co-directed a multi-institutional, interdisciplinary project, funded by DOE's natural and accelerated bioremediation (NABIR) program, to determine the effect of microbial iron and NO_{3^-} reduction on metal mobility within anaerobic groundwater.

"Through my Ph.D., I became an expert on the effect of microbial sulfate reduction on metal geochemistry. I have expanded that knowledge to include any system where microbes may be driving geochemical processes, which is any place where life exists or may exist," said Cooper. "Whether they are in an estuary, the deep subsurface, or the vadose zone of an arid sagebrush steppe, microbes and other biota drive the processes of chemical transformations."

D. Craig Cooper

At the INEEL,Cooper is applying his understanding of biotic-geochemical interactions to fundamental examinations of how microbial activity, extended time frames, and periodic wetting cycles affect speciation and the partitioning of metallic contaminants and the coupled processes controlling their ultimate fate.

"Working with physical chemists, hydrologists and microbiologists has taught me a whole new perspective. I find I have a lot to offer as a bridge between the different worlds," said Cooper.

In Cooper's opinion, he has learned more in one year at the INEEL than he would have in a similar position at a university. "The work here is so much more inherently interdisciplinary," said Cooper. "That can happen in a university setting, but here it is an integral part of the approach."

Though he was offered other opportunities, Cooper accepted the INEEL position because of the interesting subject matter and to get in on the ground floor of a growing research initiative. "The things I've enjoyed the most about the INEEL are the dynamism of the people, and the coupling of geochemistry and microbiology," said Cooper. "I feel like I came to the right place at the right time."

> **" I feel like I came to the right place at the right time."**
>
> *— C. Cooper, INEEL microbial geochemist*

Cooper earned a B.S. in Chemistry from Clemson University in South Carolina, and a Ph.D. in Chemical Oceanography from Texas A&M University. His research interests revolve around the role microorganisms play as geochemical reagents, which alter metal geochemistry by inducing changes in solution and surface properties. As a principal scientist at the INEEL, he is also supporting efforts to determine how microorganisms in the sediments at the INEEL's Radioactive Waste Management Complex affect carbon-14 and uranium transport.

Contact: D. Craig Cooper, Ph.D.
(208) 526-5395
coopdc@inel.gov

Exploring NAPL Behavior

What happened to the nonaqueous-phase liquids (NAPLs) at DOE's Hanford Site? The predictive models show they should have drained away, the result of gravity.

Unfortunately, field observations have proven the predictive models wrong, both at Hanford and at other DOE sites with NAPL contamination.

Figure 1. INEEL geoscientist Robert Lenhard with an apparatus he designed to measure the fluid saturation and pressure of two- and three-phase systems.

In Hanford's case, the discrepancy between the field observations and predictive models is large. "Modeling and field investigations only account for about 35 percent of the NAPL disposed of at Hanford," said Robert Lenhard, a geoscientist and INEEL Subsurface Science Initiatives Geosciences discipline lead. "One theory is the NAPL that is unaccounted for is held in the vadose zone as residual NAPL."

Lenhard, well-known for his work in multiphase fluid flow and chemical transport phenomena, has focused on subsurface NAPL behavior since he joined the INEEL in 2001. He and other scientists have developed numerical models to help predict NAPL behavior in three-phase (air-NAPL-water) systems. These models are based on understanding the "constitutive relations" among relative permeability (k), saturation (S) and pressure (P), commonly referred to as k-S-P constitutive theory.

As currently used in the numerical models, most constitutive theory predicts that DNAPL will completely drain from the vadose zone over time. This is contrary to laboratory and field

Figure 2. The DNAPL carbon tetrachloride was pulsed into an experimental flow cell, which contained soil layers representative of those at the Hanford site. The DNAPL's redistribution is shown after two days (left) and after 21 days (right).

observations, as in the case of the Hanford site. Lenhard and his colleagues have been working to improve the theory used in the numerical flow and transport codes to address the theory's deficiency and better predict residual DNAPL.

Lenhard's first step was to begin refining the fundamental understanding of the k-S-P relationship and the pore-scale behavior governing NAPL retention. He built and automated a state-of-the-science measuring apparatus (see Figure 1).It is capable of measuring the fluid saturation and pressure of two- and three-phase systems and quantifies the relationship

> ***" Modeling and field investigations account for only about 35 percent of the NAPL disposed of at Hanford. One theory is the NAPL that is unaccounted for is held in the vadose zone as residual NAPL."***
>
> *— R. Lenhard, INEEL geoscientist and SSI Geosciences discipline lead*

between capillary pressures and fluid saturation. Lenhard is using the apparatus to study residual DNAPL and to quantify S-P relations as a function of saturation-path history.

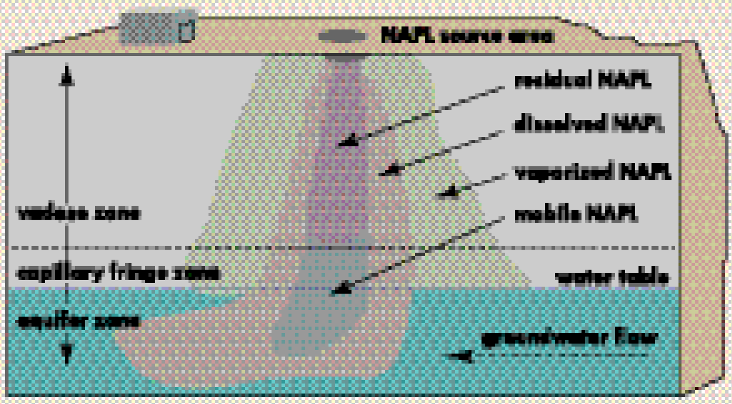
Lenhard also has been working with geoscientist Martinus Oostrom of Pacific Northwest National Laboratory (PNNL) to learn more about residual NAPLs. They conducted a meso-scale experiment at PNNL that used a flow cell 170 cm long by 90 cm high by 6 cm wide. The cell was filled with soils similar to those at the Hanford site, including sand and a layer of caliche. (See Figure 2.)

In their experiment, carbon tetrachloride (a DNAPL) was pulsed into the flow cell and allowed to gravitate downward from the surface through the sand and into the caliche

(NAPL behavior continued on page 8)

NAPLs in a Nutshell

An illustration of NAPL contamination in near-surface soils resulting from an intermittent release.



Organic liquids that are immiscible with water are commonly referred to as non-aqueous phase liquids (NAPLs). NAPLs can be either lighter than water (LNAPLs) or heavier than water (DNAPLs). Figure 1 shows an illustration of a NAPL release and its migration path in the vadose, capillary fringe and aquifer zones.[1]

NAPLs can move in a non-aqueous liquid phase, an aqueous phase, and a gas phase. Their lateral and vertical migration are affected by their own properties and properties of the soil. The movement of air, NAPL and water in the vadose zone occurs as three-phase flow. The movement of NAPL and water below the water table (in the aquifer zone) occurs as two-phase flow.

NAPLs that occupy wedges in the pore spaces in the soil, or are a thin film on a water surface, are commonly known as residual NAPLs and are relatively immobile.

LNAPLs tend to reside above the water table and if their accumulations are high, may depress the water table.

DNAPLs generally travel through the largest pore spaces and can penetrate below the water table, making them hard to locate. Predicting DNAPL movement is difficult.

NAPLs generally have some slight solubility in water despite being considered immiscible with water. Dissolved NAPL components can move with water to contaminate groundwater.

Volatilized NAPLs (in a gas phase) can move rapidly through pore spaces due to diffusion and changes in atmospheric pressure. High-pressure weather systems generally push NAPL vapors deeper into the subsurface; low-pressure weather systems generally pull the vapors from the subsurface. Because of spatial differences in gas density, high DNAPL vapor concentrations can accelerate vapor movement and can quickly contaminate groundwater.

1. *Guarnaccia, J; G. Pinder; and M. Fishman.* NAPL:Simulator Documentation. *1997, U.S. Environmental Protection Agency, EPA/600/SR-97/102.*

(NAPL behavior continued from page 7)

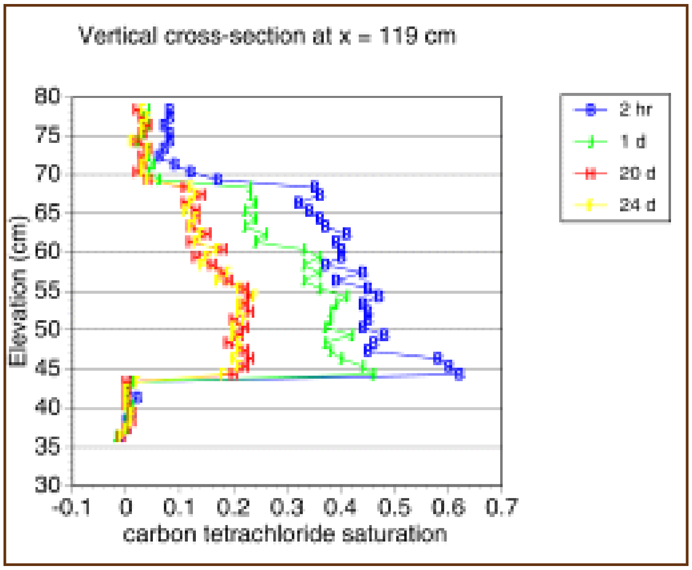


Figure 3. A dual energy gamma scan of a specific cross-section of the flow cell shows the development of carbon tetrachloride saturation over time.

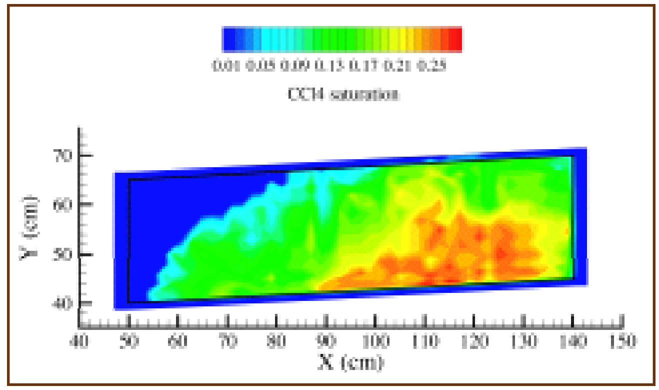


Figure 4. A dual energy gamma scan shows the development of carbon tetrachloride distribution after apparent static conditions were obtained.

layer. A dual-energy gamma-radiation attenuation system nondestructively measured the movement of the DNAPL and water in the cell. (See Figure 3.)

After about 20 days, the experiment reached a static condition. Measurements showed the caliche layer retained twice the residual NAPL as the sand. (See Figure 4.)

Then, to simulate precipitation and aqueous-phase disposal events, water was applied to the surface. The researchers again waited until the

" The only way to develop a better model is to continue conducting experiments at a scale where field-scale contaminant behavior can be meaningfully replicated."

— R. Lenhard, INEEL geoscientist and SSI Geosciences discipline lead

system reached a static condition. Measurements of the DNAPL and water saturations showed that nearly 70 percent of the DNAPL remained in the caliche, even after significant water infiltration.

"The meso-scale test apparatus at PNNL was invaluable in adding to our understanding of NAPL behavior," said Lenhard. "With it, we were able to quantitatively observe the movement of NAPL through time."

In future experiments, Lenhard and his colleagues plan to evaluate their hypothesis: Residual NAPLs (including DNAPLs) are dependent on water and NAPL saturation-path histories, and residual NAPL is a function of soil water content.

Lenhard also plans to continue working to develop predictive models that account for residual NAPL saturation. "The only way to develop a better model is to continue conducting experiments at a scale where field-scale contaminant behavior can be meaningfully replicated," said Lenhard.

"One of the reasons I joined the INEEL team was the focus on meso-scale experimentation. For multiphase flow and the problem of residual NAPLs, I think having the capability to conduct meso-scale experimentation is crucial."

Note: This research is funded by the INEEL's Laboratory Directed Research and Development (LDRD) program. It is being conducted by: Robert J. Lenhard, Ph.D. (from the INEEL) and Martinus Oostrom, Ph.D. (from PNNL).

Contact: Robert Lenhard
(208) 526-4767
lenhrj@inel.gov

Fellowships and Internships
— *Supporting SSI's Research Portfolio*

The INEEL's Education and Research Initiatives (ERI) program has been one of the best-kept secrets in academia, but it won't be for long. If you are a faculty member, post-doctoral candidate, graduate student or undergraduate, you may get paid to work in your field of interest through the INEEL's university programs. And for graduate students, the pay isn't bad.

"I just stumbled onto it, and it turned out to be a dynamite deal," said Mary Kauffman, a student at Montana State University. She recently finished an interdisciplinary master's degree in geology and microbiology at Idaho State University through an INEEL fellowship and is now pursuing a Ph.D. "I'm actually being paid to do my *own* research, and I have access to both university and national laboratory facilities," said Kauffman.

There are five programs offering opportunities in subsurface science, ranging from practicums for undergraduates to visiting faculty positions for professors on sabbatical. Each program's purpose is the same — to promote successful collaboration between academia and the INEEL's scientists and engineers, and improve the exchange of ideas, information and technology. Applicants need to meet the specific criteria required by each program, but the key to participating is connecting with an INEEL researcher to identify areas of common research interest and funding availability.

"Once I had a contact at the INEEL, it was a simple process to connect with the right people to complete the arrangements," said Teresa Culver, an engineering professor spending her sabbatical as a visiting faculty fellow from the University of Virginia at Charlottesville.

Charlie Ann Lovejoy, of the INEEL's ERI program, said the Lab does a lot of the work after the contact has been made. "Our job is to make the process easy for both the participants and their INEEL mentors or counterparts," said Lovejoy.

Beyond having extra hands to perform research, the INEEL and DOE get an added benefit — the program is a significant recruiting tool. "We have more than 100 researchers participating in the fellowship program each year," said Fred Gunnerson, who manages the ERI program. "The program gives both the student and the INEEL a chance to develop mutual interests. Often, the student ends up pursuing a career as a researcher at the INEEL or one of DOE's other national labs."

"Of course, not all of our programs' benefits can be described in pure academic terms," said Gunnerson. "Idaho's outdoor recreation opportunities — Yellowstone and the Tetons — are one of the intangibles that makes recruiting a bit easier."

Some ERI programs are described below by level of academic achievement, beginning with opportunities for undergraduates. More information is on the internet at **http://education.inel.gov/university/**

Practicums

Practicums are designed for undergraduate students who have finished their coursework, but have a requirement or option for a practicum to graduate from a four-year institution. The practicum's duration and potential stipend are determined by the college or university. Only one award is allowed per student.

Undergraduate Fellowships

Undergraduate fellowships offer academically eligible undergraduate students an opportunity to participate in applied research, development and application projects related to one of the INEEL's missions. These can either be a 10- to 16-week summer program, or a quarter- or half-time position during an academic semester having a duration of 15 weeks or more.

Graduate Fellowship

Graduate fellowships are designed for master's or doctoral students who would like a full- or part-time opportunity to conduct research for their thesis, dissertation, or project. Fellowships can be awarded for a period of up to 12 months and renewed for a maximum of three years, which can be nonconsecutive. Depending on the research project, participants can be located at the INEEL, their university, or both. Before submitting an application for this position, the applicant or his adviser must establish contact with an INEEL scientist or engineer who will serve as a mentor.

Postdoctoral and Postgraduate Internships

Graduates who have completed a master's or doctoral degree within the past 12 months are eligible for part- or full-time appointments focusing on high-level research in the graduate's area of expertise. Appointments are renewable, based on performance and available funding, for up to three years. The program is administered by Washington State University (WSU) through the Inland Northwest Research

(Fellowships/Internships continued on page 15)

New Geocentrifuge Arrives at the INEEL

Workers prepare a foundation for the INEEL's new 2-meter geocentrifuge at the Bonneville County Technology Center in Idaho Falls, Idaho.

There are fewer than 20 large-scale geocentrifuges in the United States, and of those, only a handful are dedicated to environmental investigations. However, before the year is over, another geocentrifuge will be available. It will be located at the INEEL's new Geocentrifuge Research Laboratory (GRL), and will primarily be dedicated to environmental research.

The components of a newly-fabricated Actidyn Systemes C-61, a 2-meter geotechnical centrifuge system, began arriving at the INEEL in May. The system will be housed in a new facility being constructed at the Bonneville County Technology Center in Idaho Falls, Idaho.

The research planned for the INEEL's new geocentrifuge will include studying subsurface movement of fluids and contaminants and the long-term performance of engineered caps and barriers.

> ***"Using the geocentrifuge to test engineered barrier and cap designs will help DOE in its assessments."***
>
> *— A. Stadler, INEEL research engineer and principal investigator for the GRL*

"Engineers develop numerical codes to assess a design's long-term performance, but the codes are not always fully supported by experimental data," said Alan Stadler, an INEEL research engineer and principal investigator for the new laboratory.

"They often have to extrapolate well into the future, sometimes as much as 10,000 years. Using the geocentrifuge to test engineered barrier and cap designs will help DOE in its assessments."

Using a geocentrifuge's high-gravity environment to accelerate the effects of gravity on fluid flow and contaminant transport is a natural extension of its capabilities. Most of the other geocentrifuges in the United States are used primarily for geotechnical work, testing strength and mechanical properties of geological materials, and simulating the effects of gravity and earthquakes on structural properties.

After all the components have been installed in the new laboratory, the first step will be to calibrate the system.

"We plan on working with Trish Culligan at the Massachusetts Institute of Technology," said Stadler. "She will use the geocentrifuge located there to study colloid migration. Then, we will replicate her experiments at our new facility to both validate her results and our calibration efforts."

Hideo Nakajima, an SSI research engineer and recent doctoral graduate, will work with Stadler to calibrate the system. He will conduct the first experiments with the new system — one-dimensional column tests to determine hydraulic properties. The results will be used to calibrate the geocentrifuge system's instruments and validate prior work done on the INEEL's smaller scale centrifuge, the unsaturated flow apparatus.

> ***"Though we'll be ready to throw the switch this year, we'll still be developing new experimental packages."***
>
> *— A. Stadler, INEEL research engineer and principal investigator for the GRL*

While Stadler leads the cap and barrier efforts, Nakajima will lead the new laboratory's environmental research program. He and Stadler will work together to prepare the wide variety of novel and sophisticated instrumentation required for this work.

"Though we'll be ready to throw the switch this year, we'll still be developing new experimental packages," said Stadler. "For example, we'll need new sensors. Most are not designed to withstand a high-g environment. Fortunately, one of the INEEL's strengths is sensor development and it is much easier to develop instruments here than at a university."

Stadler said the timing of the new facility is good because it coincides with the development of improved technologies. "Some miniaturization and wireless technologies have matured to a degree where they can be integrated into our experimental packages."

After the new laboratory is operational Stadler expects it will remain busy. "When we are not running geoenvironmental experiments for DOE and the scientific user community, we expect the system's geotechnical capabilities will keep it spinning."

Note: The INEEL (managed and operated by Bechtel BWXT Idaho, LLC) is using corporate funded research and development (CFRD) funds for the geocentrifuge and its installation. DOE's Environmental Systems Research and Analysis (ESRA) program is funding the initial calibration and instrument development.

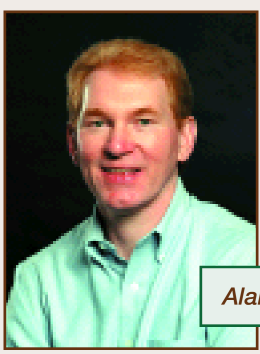
Contact: Alan Stadler, Ph.D., P.E.
(208) 526-4784
stadat@inel.gov

SSI Adds New Research Talent to Operate Geocentrifuge

Alan Stadler

Alan Stadler joined the INEEL in February 2002 as the principal investigator for the SSI's new 2-meter Geocentrifuge Research Laboratory. Stadler said he was drawn to the position by the startup nature of the SSI program and the chance to set up a new geocentrifuge. "A 2-meter geocentrifuge doesn't come online every day…or even every decade," he said. "It's rare for a scientist to be given a blank slate like this. It's a once-in-a-career opportunity."

Stadler's role includes developing the physical infrastructure of the new facility, and initiating and facilitating research activities,


Alan Stadler

especially in the area of caps and barriers. "One of my jobs will be to reach out to the broader research community to make this a true user facility," said Stadler. "Having a large geocentrifuge in the Northwest is a great resource, particularly for regional universities. It is important to get the word out. I would like to see a lot of peer-reviewed publications produced as a result of this resource."

By hiring so many SSI staff from academia, Stadler thinks the INEEL is sending a strong signal it wants to increase its interaction with universities and boost the number of peer-reviewed publications coming from the Lab.

"There is a lot of peer-review quality research going on at the INEEL, but a lot of it has gone unrecognized because publication isn't emphasized as much as it is in academia," said Stadler. "I think that will be changing in upcoming years, particularly in the field of subsurface science."

Stadler's primary area of expertise is geotechnical engineering. He has a full complement of degrees in civil engineering — both bachelor's and master's degrees from Ohio State University and a doctorate from the University of Colorado (CU) at Boulder. Stadler's dissertation involved using a 6-meter geocentrifuge and other geotechnical laboratory facilities. He later moved to the University of North Carolina in Charlotte where he spent five years as an assistant professor in the Department of Civil Engineering. Stadler is a registered Professional Engineer in both North and South Carolina and has more than seven years of consulting engineering experience.

Hideo Nakajima

Hideo Nakajima accepted a postdoctoral internship at the INEEL's SSI Geocentrifuge Research Laboratory in February 2002. Nakajima is responsible for building the new


Hideo Nakajima

"The major attraction of using geocentrifuges to study NAPL movement is their ability to reduce both time and geometric scales and to provide data to verify the results of numerical models. The key challenge is to understand the scaling relationships for complex problems."

— H. Nakajima, INEEL engineer and postdoctoral intern

laboratory's research program and helping researchers set up their experiments.

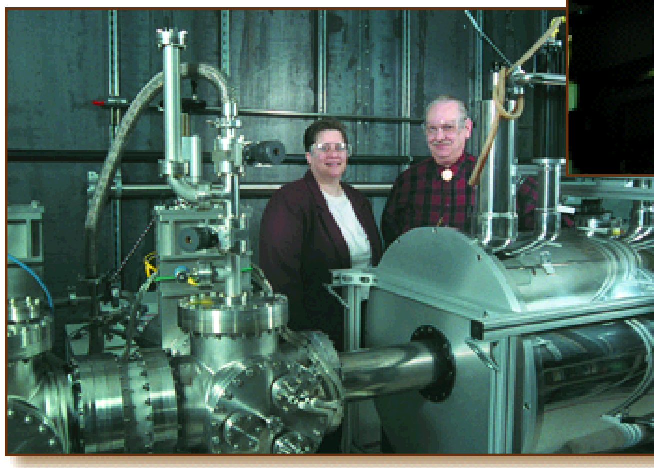
His new role will also allow him to pursue his research interests — developing experimental techniques for multiphase flow. Besides using the

(Research talent continued on page 16)

Microbes, Minerals and Mass Spectrometry

Mary Kauffman

Researchers at the INEEL are using new instruments and finding new ways to use existing instruments to learn more about interactions of microbes and minerals in the subsurface.



The INEEL's Jill Scott and Paul Tremblay with the LOCI, the INEEL's unique surface fluorescence and chemical imaging instrument.

"Ninety-five percent of the microbial organisms in the subsurface are attached to something. Their interactions with mineral surfaces affect them dramatically. They can have different morphologies, conduct different chemical reactions, and even express different genes," said INEEL graduate fellow Mary Kauffman. Getting at the mineral-microbe relationships has required Kauffman to apply a novel set of instruments to the problem.

> *"Culturing microbes from groundwater samples tells very little about how microbes live. We need to know about the other 95 percent — how they interact with minerals, and how that interaction affects their capacity to transform contaminants."*
>
> — M. Kauffman, INEEL graduate fellow and microbiologist

"Culturing microbes from groundwater samples tells very little about how microbes live," said Kauffman. "It only provides about 5 percent of the answer. We need to know about the other 95 percent — how they interact with minerals, and how that interaction affects their capacity to transform contaminants."

Kauffman, a doctoral student at Montana State University in Bozeman, focused her efforts on basalts and the microbes that have an affinity for them. Some of these microbes can produce toluene-oxidizing enzymes capable of breaking down many organic contaminants.

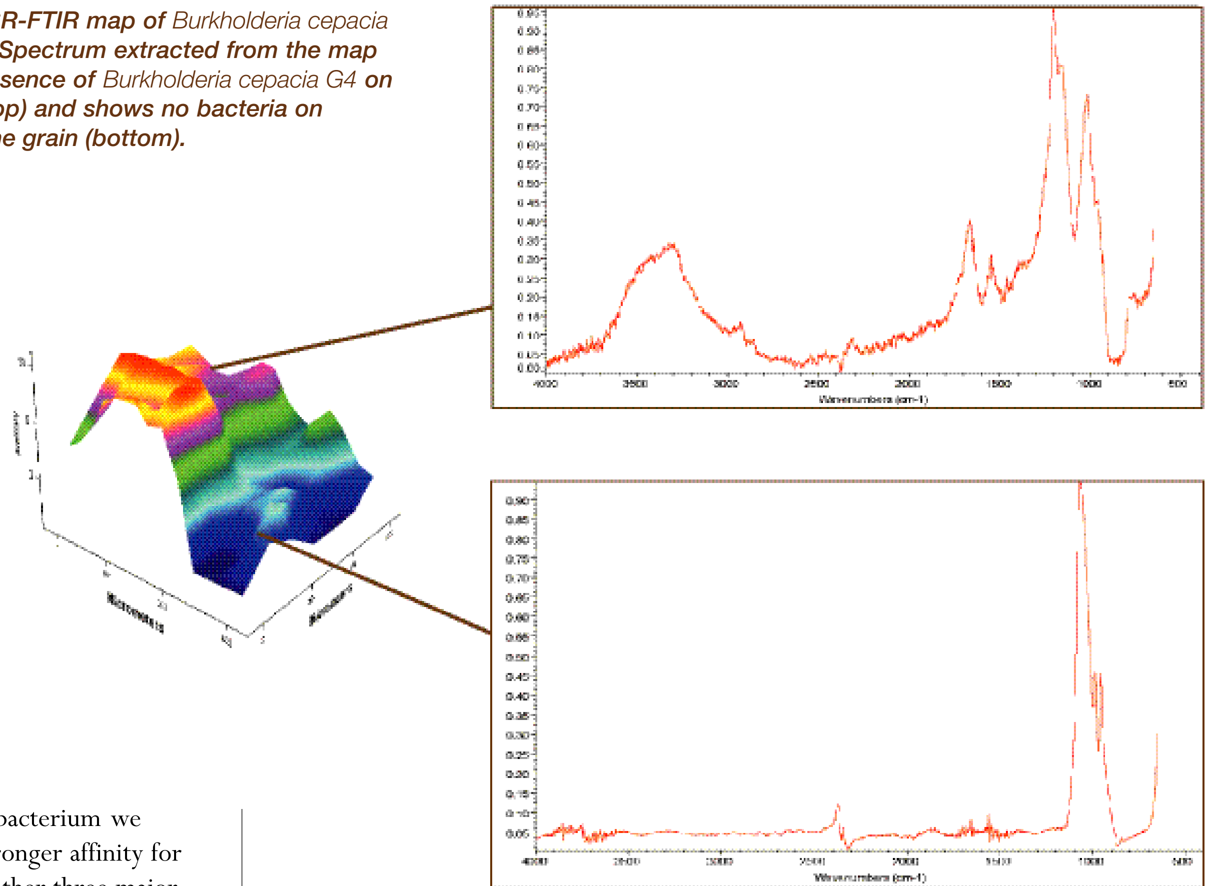
She collected basalt samples with extremely fine-grained and mineralogically heterogeneous minerals for the research. "Because the microbes are discriminating, studying them is not as simple as putting isolated mineral samples in cultures and seeing which ones grow more colonies," said Kauffman. "You have to use real rock samples because microbial preferences in native samples differ from using laboratory grade mineral crystals."

To understand how the bacteria are spatially distributed on the basalt's surface, Kauffman worked with Hoi-Ying Holman, a research scientist at Lawrence Berkeley National Laboratory (LBNL). They conducted an in situ examination of the colonized basalt using Synchrotron Radiation-Based Fourier Transform Infrared (SR-FTIR) spectromicroscopy at the LBNL's Advanced Light Source. A 10-micron, nondestructive infrared beam was focused on the surfaces, allowing the spatial distribution and mineral preferences of the bacteria to be identified.

> *"The bacterium we tested had a much stronger affinity for plagioclase than the other three major mineral components of basalt."*
>
> — M. Kauffman, INEEL graduate fellow and microbiologist

The microbial population demonstrated a clear mineral preference. "We grew cultures in the presence of fine-grained basalt,"

Figure 1. An SR-FTIR map of** Burkholderia cepacia G4* ***on basalt. Spectrum extracted from the map shows the presence of** Burkholderia cepacia G4* ***on plagioclase (top) and shows no bacteria on adjacent olivine grain (bottom).



said Kauffman."The bacterium we tested had a much stronger affinity for plagioclase than the other three major mineral components of basalt." (See Figure 1.)

Jill Scott, an INEEL chemist, was able to confirm Kauffman's results using the INEEL's customized Fourier transform mass spectrometer (FTMS) coupled with an automated laser scanning system known as the Laser-based Optical and Chemical Imager (LOCI).

"After Mary described her research problem, I asked her for some samples so we could test our spectrometer's new chemical and optical imaging systems," said Scott."The best way to develop instrumentation is to make sure it can run real samples."

Scott has been working with INEEL instrument developer Paul Tremblay to develop the LOCI system. The system both optically and chemically images a sample.[1] The spatial resolution of LOCI is adjustable and virtually unlimited."Right now, the laser beam focusing optics restrict resolution to a 2-micron diameter. However, when the optics have been upgraded, the instrument will be capable of much finer focusing resolution," said Tremblay.

"The LOCI system is unique in its sophisticated laser-focusing abilities.The laser can repeatedly return to an exact spot on the sample... providing true depth-profiling capability."

— J. Scott, INEEL chemist

The optical imaging component takes advantage of fluourescent surface mapping so colonies located on the sample can be targeted for interrogation by the LOCI using stained or marked microbes that fluoresce. The laser used for the FTMS can then repeatedly and precisely ablate the surface to obtain the chemical image by mass spectrometry.

"The LOCI system is unique in its sophisticated laser-focusing abilities," said Scott."The laser can repeatedly return to an exact spot on the sample until it gets down to the underlying mineral surface, providing true depth-profiling capability."

The LOCI's confirmation was important because the SR-FTIR technique can be limited if the biofilm grows so thick it obscures the spectrum used to identify the underlying mineral. "Because LOCI analyzes the samples by depth-profiling, the thickness of the biofilm is not a hindrance," said Scott.

Using the spectra obtained from each reading, the software creates a chemical image made up of individual

(Microbes continued on page 14)

(Microbes continued from page 13)

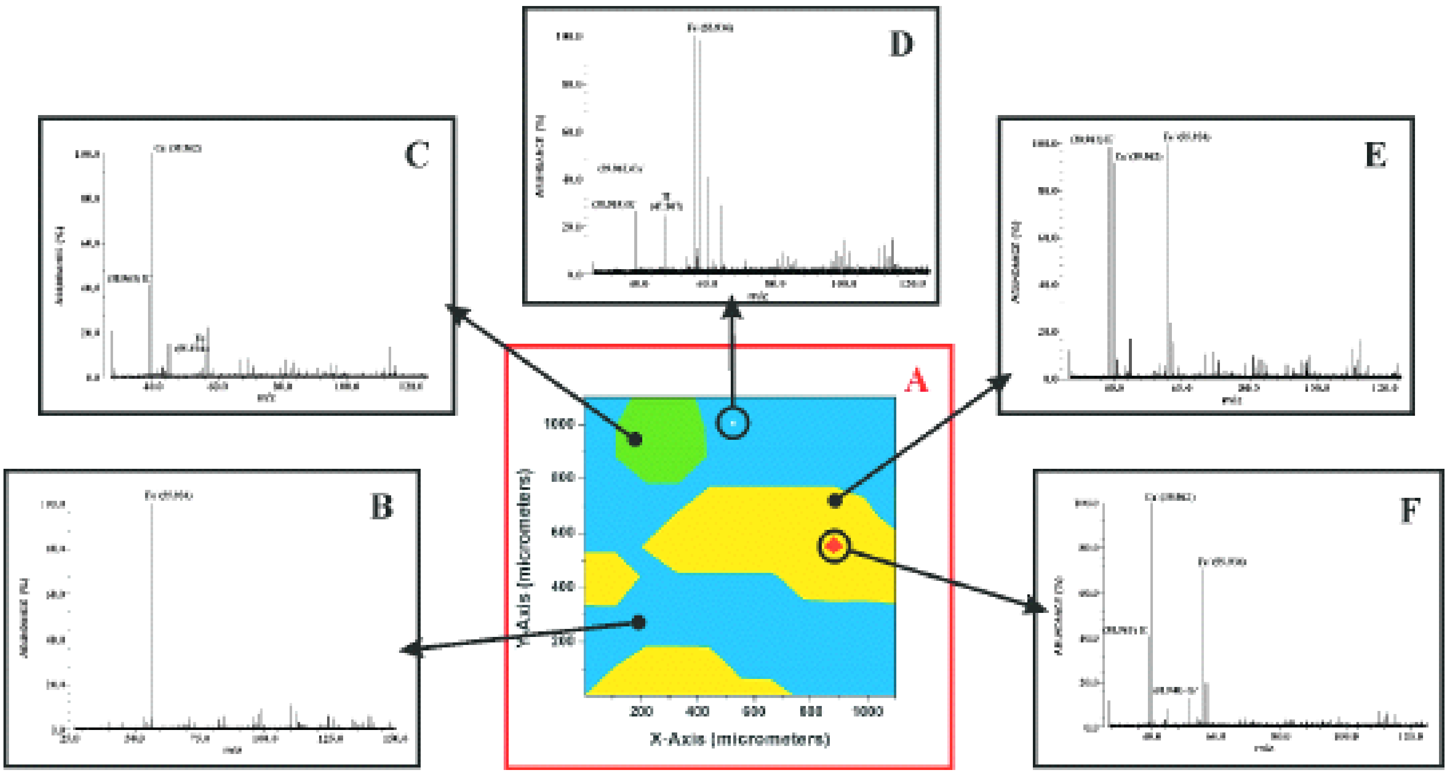


Figure 2. Chemical image of basalt: (A) Image of ~1100 x 1100 mm area of basalt thin section. Typical spectra of mineral types: (B) Olivine, (C) Plagioclase, (D) Ilmenite, (E) Augite, and (F) Augite with chromium. All spectra are from single laser shots.

pixels each having its own spectral reading (see Figure 2). The chemical image that results from single or multiple passes is made possible through precise automation and the system's own fuzzy-logic inference engine, which was developed by INEEL electrical engineer Tim McJunkin. LOCI acquires approximately 7,200 files per hour, which can be interpreted in about 20 minutes, to identify the specific compounds on the surface.[2] "Without the inference engine, classifying the enormous number of files LOCI can create in a day would be a daunting task," said Scott.

In future investigations, Kauffman and Scott want to examine how the mineral surfaces change as a result of microbial-mineral interaction. "We know microbes are dramatically affected by their interactions with mineral surfaces," said Kauffman.

"But the same is true for the minerals, which themselves are altered by their interactions with microbes. Because the dynamic of contaminants in the subsurface is affected by both, this work is really fundamental."

Interactions affecting uranium and arsenic mobility are of particular interest to both Scott and Kauffman. "We know uranium and arsenic have partitioning affinities for certain minerals," said Scott. "Now that we are capable of studying microbial affinities, the next step is to examine the combined interactions and learn how they affect contaminant transformations and mobility."

1. *Scott, J. R.; Tremblay, P. L.* Rev. Sci. Instrum. *2002, 73, 1108-1116.*
2. *McJunkin, T. R.; Tremblay, P. L; Scott, J. R.* JALA *2002, in press.*

Note: Kauffman's research on microbial affinities for minerals is funded by DOE's Environmental Systems Research and Analysis (ESRA) program. The development of the LOCI is funded by the INEEL's Laboratory Directed Research and Development (LDRD) program.

Contacts: Mary E. Kauffman
(208) 526-2684
kaufme@inel.gov

Jill R. Scott
(208) 526-0429
scotjr@inel.gov

(Fellowships continued from page 9)

Alliance (INRA). Full-time interns receive a complete WSU benefits package, including a relocation allowance. More information on the internship program can be found at **www.inel.asp.wsu.edu**

Faculty Fellowship

Faculty Fellowships offer participants the opportunity to develop a long-term collaborative research relationship with the INEEL. They also enhance the teaching and research capabilities of the participants while sharing their academic experience and abilities with the INEEL. Full- or part-time appointments are offered at the INEEL, or on the campus of a college or university. Applicants must establish a collaborative research effort with an INEEL principal investigator. Applicants are selected based on their qualifications and the strength of their research proposal. Faculty sabbaticals are encouraged.

Contact: Anne Sneed
(208) 526-3990
sneea@inel.gov

Current Participants in INEEL's Education and Research Initiatives Program

Faculty Fellowship

Teresa Culver, Associate Professor
University of Virginia at Charlottesville

Teresa Culver has spent the last academic year at the INEEL, away from her position as Associate Professor of Civil Engineering at the University of Virginia. The faculty fellowship has given Culver the opportunity to focus on her research, developing an optimization model for engineering pump-and-treat systems.

Teresa Culver

"You can get isolated in academia, and engineering is inherently an applied field," said Culver. "As an engineering researcher and instructor, I have a responsibility to have experience in applying research to a real-world engineering problem. So, I'm working on optimizing design techniques for groundwater remediation."

Culver pursued the opportunity after learning about INEEL's academic programs at an American Society of Civil Engineers (ASCE) meeting. "Knowing someone at the Lab and finding areas of intersecting interest is the key," said Culver. "The rest of the process is pretty straightforward. I submitted a research proposal to my school's sabbatical program and to the INEEL's Education and Research Initiatives program. Once approved, the funding and other administrative issues were fairly transparent to me."

Postdoctoral Fellowship

Birsen Canan, Ph.D.
Colorado School of Mines

After finishing her doctorate, Birsen Canan began postdoctoral work at Boise State University's Center for Geophysical Investigation of the Shallow Subsurface (CGISS). But she continued searching for work that more closely matched her area of interest.

Through her advisor at the Colorado School of Mines, Canan learned the INEEL was seeking postdoctoral researchers. She contacted Russ Herzog, the SSI Geophysics Discipline Leader, and they had several conversations about research interests. She later met Herzog while presenting a paper at the Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP).

Birsen Canan

"The work the INEEL was pursuing matched my interests very closely. They liked my research proposal, so here I am," said Canan. "Now I'm two years ahead of where I thought I would be in my career and excited to be doing my own research."

The process has been a bit more difficult for Canan, who is a Turkish citizen. "I have been the perfect guinea pig. I was the first person accepted into postdoctoral fellowship program after Washington State University in Pullman began managing the program," said Canan. "And as a foreign national working at a government laboratory, my situation has posed a few additional challenges. But I have received a lot of personal attention and everybody in security has been helpful."

Canan is currently the technical lead for a project researching the feasibility of using nonlinear complex resistivity (NLCR) to noninvasively map and monitor microbiologically mediated reactions in contaminated, heterogeneous subsurface environments. The specific biological

(Fellowships/Internships continued on page 16)

(Fellowships continued from page 15)

reaction of interest is the reduction of hexavalent chromium to trivalent chromium by indigenous bacteria.

Graduate Fellowship

Mary Kauffman, M.S.
Idaho State University; pursuing a Ph.D. at Montana State University

Mary Kauffman's interest in coupling geology and microbiology is a perfect fit with the INEEL's focus on subsurface science. "Having the ability to do master's research as part of my job is almost too good to be true," said Kauffman. "My last fellowship completed my M.S., and now I have a fellowship to get a Ph.D. It's great."

Kauffman said one of the program's greatest benefits is having access to instruments like the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) and the INEEL's Laser-based Optical and Chemical Imager (LOCI). These instruments have allowed her to pursue very specialized research interests that might not be available at most universities.

"The best part has been working with established scientists at the INEEL. They have been extremely generous in sharing their experience and teaching me all aspects of what it takes to be a professional scientist. I can't thank them enough for all I've learned."

Kauffman is currently studying the affinity of certain microbes — those with useful attributes for environmental remediation — for particular mineral surfaces (see article on page 12).

(Research talent continued from page 11)

large-scale geocentrifuge to study LNAPL movement in subsurface environments, Nakajima is looking forward to the opportunity to work with the SSI's Bob Lenhard, who is well-known for his work in modeling multiphase fluid flow in the vadose zone.

"The major attraction of using geocentrifuges to study NAPL movement is their ability to reduce both time and geometric scales and to provide data to verify the results of numerical models," said Nakajima. "The key challenge is to understand the scaling relationships for complex problems."

Nakajima pursued his doctorate in civil and environmental engineering at University of California at Davis, which is known for its pioneering work in centrifuge modeling of contaminant transport. While there, he used a 1-meter geocentrifuge.

Ultimately, Nakajima looks forward to performing his own experiments. "Working with people in different and yet complementary disciplines will make my own research much more productive," said Nakajima.

Contact: Hideo Nakajima
(208) 526-4786
nakah@inel.gov

SUBSURFACE
— SCIENCE —
INITIATIVE

Subsurface Science Initiative
INEEL MS 2214
P.O. Box 1625
Idaho Falls, ID 83415-2214

Address Service Requested

http://subsurface.inel.gov

PRESORT STD
U.S. POSTAGE
PAID
IDAHO FALLS, ID
PERMIT NO. 73